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DIFFUSION IN COMPLEX LIQUID SURFACES - A MONTE CARLO STUDY

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Abstract: The temperature and concentration dependences of the surface diffusion coefficient of ions in a 2-D complex liquid surface is investigated using Monte Carlo Simulaion. The surface of the solution is considered to be composed of two ions embeded in the sea of n point dipoles representing water molecules. The interactions considered in the chosen system are charge-charge, charge-dipole, dipole-dipole. The temperature dependence of the diffusion coefficient shows the existence of a T_c, on two sides of which the surface diffusion coefficient behaves oppositely. There is another temperature $T_p < T_c$, where the nature of variation of the diffusion coefficient again changes.

Key words: 2D-electrolyte solution, Diffusion Coefficient, Monte Carlo Simulation, Temperature Dependence, Concentration Dependence.

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1. Introduction

Surface is the exterior-most part of any solid or liquid system through which it interacts with the environment. The structure of the liquid surfaces

at the molecular level is very poorly understood because of the inherent complexity of the system arising out of the continuously changing arrangement of different types of constituent particles. Moreover, the lack of nearest neighbours on one side of the surface particles (which may be ions, or atoms or molecules) make some chemical bonds to dangle into the space outside the system and available for chemical reactions. Due to the presence of these dangling bonds the dynamic properties of the surfaces differ drastically from that inside the same bulk.

Out of the broad spectrum of liquids,we have selected the electrolyte solutions for our study. Electrolyte solutions are of importance in a wide range of scientific contexts and as such have attracted considerable theoretical and experimental effort over the years [1]. Nevertheless, there is still no work on the 2D (interface or surface) - electrolyte systems. To study the dynamic properties of the surfaces we have chosen diffusion as a tool and the method we are presently adopting is that of computer simulations, which being neither experiment nor theory - can take over the task of both. Moreover, the computer simulation results for the complicated liquids like aqueous electrolyte solutions, which has not yet been treated analytically, throw new light towards the understanding of the system. Here we report the temperature and concentration dependence of the diffusion coefficient in a surface of aqueous electrolyte, obtained by Monte Carlo Simulation.

2. Methodology

The surface with which we are dealing is really a very complicated one. In fact, there is still no generally agreed structural model of electrolyte solutions. Till now the best as well as the simplest way to represent a 3D aqueous electrolyte system is to treat them as a mixture of hard spheres of equal diameters and charges embeded in a sea of point dipoles [2]. However, to start with we consider the surface of electrolyte solution to be composed of point charges embeded in a sea of point dipoles (representing water molecules). Diffusion of charged particles in such a 2D system has been studied by Monte Carlo Simulation using the standard METROPOLIS algorithm [3]. A 10 x 10 square lattice is taken to simulate the system. Two ions (one +ve and one -ve) and n water molecules are placed randomly at the lattice sites. n is varied to generate electrolyte solution of different concentration (num-

ber density). These particles are at liberty to move randomly inside the lattice. Periodic boundary conditions are used to minimise the size effect. Only nearest neighbour interactions are considered. 10^5 Monte Carlo Steps (MCS) per particle are allowed to reach the equilibrium configuration. The effective interactions existing in the system are charge-charge, charge-dipole, dipole-charge, dipole-dipole and charge-quardrupole. Among those the interactions which we consider in this work are -

$$\begin{aligned}
\text{Charge} - \text{charge} \quad & \phi_{cc}(r_{ij}) = q_i q_j |r_{ij}|^{-1} \\
\text{Charge} - \text{dipole} \quad & \phi_{cd}(r_{ij}) = -q_i \mu_j \nabla(r_{ij}^{-1}) \\
\text{Dipole} - \text{dipole} \quad & \phi_{dd}(r_{ij}) \quad -(\mu_i.\nabla)(\mu_j.\nabla)(r_{ij}^{-1}) \\
\text{Total energy} = \phi_{cc} + \phi_{cd} + \phi_{dd}
\end{aligned}$$

where r_{ij} is the distance between two charges, q_i, q_j the charges at ith and jth sites, μ_i, μ_j are dipole moment of the dipoles at ith and jth sites.

The state parameters used in the simulation procedure are listed in Table 1. The values of μ and q correspond to the dipole moment of water and the charge of a monovalent ion. As the system is very complicated, our work is still continuing so as to reach the real physical situation. However, we are reporting here the temperature and concentration dependence for a very simplified version of the system.

Table I

MOLECULAR PROPERTIES			
Charge of ion		1.6×10^{-19}C	
Dipole moment of the solvent		1.87D	
CONFIGURATION SAMPLING PARAMERTERS			
Max. displacement per configuration		0.05 times box length	
Max. rotation of dipole per config.		4.5^o in θ	
CONCENTRATION			
Number of ions	2	2	2
Number of dipoles	40	53	66
Total number of particles	42	55	68

3. Results and Discussions

The surface diffusion coefficients of the positive charge have been calculated over the 'Monte Carlo' temperature T_m ranging from 10^{-6} to 10^{6} for three different values of n - 40, 53, 66. The results are shown in fig.1. Both T_m and the surface diffusion coefficients are in arbitrary units. The log T_m versus surface diffusion coefficient curve shows following interesting features
(1) The surface diffusion coefficients for all the three systems are more or less same in the range $logT_m = 1$ to 6.
(2) The surface diffusion coefficient below $logT_m = -1$ decreases upto $T_m = T_c$ and this T_c decreases as we decrease the number of water molecules in the lattice i.e. with the decrease of the number density of water molecules.

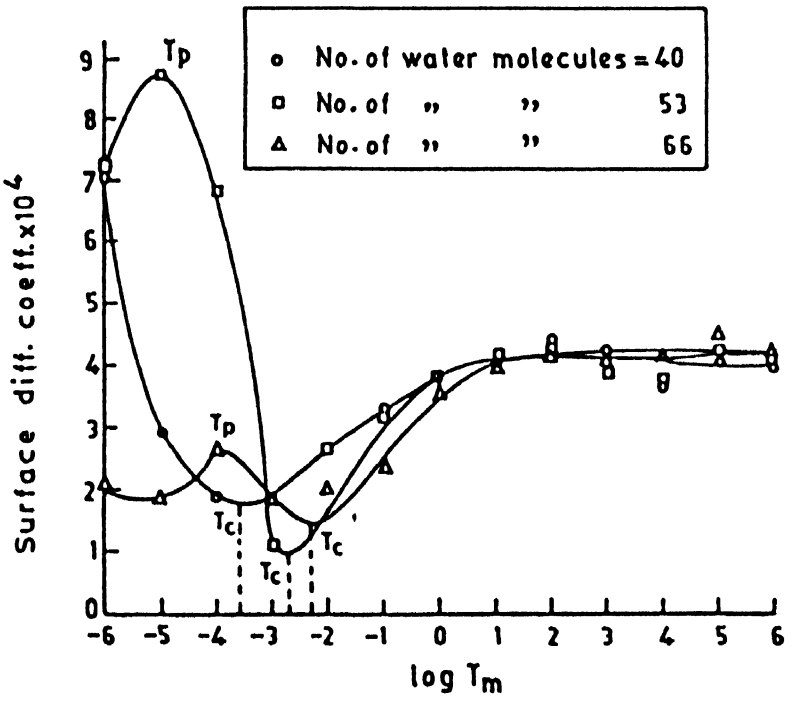

Fig.1 Temperature (Monte carlo) dependence of the surface diffusion coefficient of electrolyte solution at different concentrations

(3) If the temperature is further decreased below T_c, the change in the surface diffusion coefficient profile is reversed. It then starts increasing upto a certain value T_p and then again decreases. With the increase of number of water molecules in the lattice, the value of T_p shifts towards zero temperature. T_p for the two systems consisting of 66 and 53 water molecules respectively are shown in figure 1. For the system having 40 water molecules it is not observable in figure, but from the trend of the curve representing the system, it may plausibly be anticipated that T_p lies in the range of 10^{-8} to 10^{-7} T_m.

All these features are very interesting as they are pointing towards the occurance of some peculiar types of phase transitions and are to be investigated in detail.

4. Conclusion

The system we have chosen comprises of two oppositely charged ions embeded in a sea of water molecules. Water itself is a strongly polar liquid, dipole moment of a single water molecule is 1.87 D. Thus the presence of a charge of the order of 1.6×10^{-19}C localised on an ion will produce a major perturbation in the local structure. This perturbation is so marked that it can produce a hydrated ion. Furthermore the force law for ion-ion interaction is long ranged so that the distribution of ions with respect to each other will depend in a complicated way on their seperation. A further difficulty is that, pure liquid water is hydrogen bonded and both its structral and dynamical properties are matters of controversy. So it would not be surprising if the simulation results based on our simplified model differ from experimental results. However at present our model and calculation are at a very embrionic stage and various modifications are being introduced so as to approach the real physical situation.

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